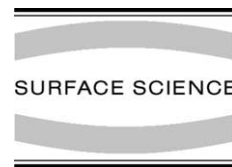




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# It's a dusty Universe: surface science in space

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## Abstract

We live in a dusty Universe! Dust is not only found in our solar system among the planets but is found in a wide variety of objects throughout the Universe, mainly in those regions between the stars known as interstellar clouds. Interstellar dust particles, which consist of cores of silicates and carbonaceous material often surrounded by icy mantles, are most probably highly irregular in shape with a size distribution from micro- to nanometers. Interstellar dust is important for many reasons, including the template it provides for surface chemical reactions that form, among other species, the most important interstellar molecule—H<sub>2</sub>. In this article, we discuss the evidence for interstellar dust, its physical and chemical properties, its role in interstellar surface chemistry, and what remains to be learned. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Models of surface chemical reactions; Models of non-equilibrium phenomena; Atom–solid interactions; Diffusion and migration; Silicon oxides; Amorphous surfaces

## 1. The Universe is dusty!

### 1.1. Introduction

Around 1784, William Herschel, the musician turned astronomer at the court of King George III, noted the existence of small regions in the sky where there appeared to be a complete absence of stars. These regions were most easily seen against the rich star-fields of the Milky Way. Herschel was struck by these apparent voids in the distribution of stars, and called them “holes in the sky”. From the evidence at the time, it was unclear whether these

“holes” were true absences of stars, as Herschel proposed, or whether—as we now know—something was obscuring the radiation from a distant star field. In fact, although Herschel’s observation was not interpreted in that way, this was probably the first indication that there is material in the space between the stars, the interstellar medium, and that this material is capable of absorbing starlight. Fig. 1 shows an apparent void in space, now known to be a rather dense interstellar cloud that is blocking the light of background stars.

The interstellar medium has been actively studied by astronomers since that time. At first, the obscuration was regarded merely as a hindrance to the observation of objects of proper astronomical concern, the stars and galaxies. Therefore, the efforts that astronomers made were simply to find

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Fig. 1. The “Black Cloud” B68. The dust particles in this dense interstellar cloud extinguish most of the background visible starlight. Dense interstellar clouds are studied at longer wavelengths, which can penetrate the dust. Permission to reproduce the figure here has been granted by ESO, which holds the copyright. Taken from web site <http://antwrp.gsfc.nasa.gov/apod/ap990511.html>.

ways of accounting for the extinction as accurately as possible, so that the properties of stars and galaxies might be accurately known. Gradually, however, it became clear that the obscuring medium was interesting in its own right [1]. A variety of observations showed that the extinguishing agents in interstellar space are dust grains of a size comparable with the wavelength of visible light. These particles not only absorb starlight quite efficiently, but scatter it, too. The absorbed radiation heats the dust grains, which then re-radiate in

the infrared to the millimeter-wave (depending on temperature): what goes in as optical radiation must come out as thermal radiation. It is now known that dust grains contribute approximately 1% of the mass of material in interstellar clouds, with a number density of dust roughly  $1.3 \times 10^{-12}$  that of the gas phase, if one assumes the “standard” grain radius of  $0.1 \mu\text{m}$ . The gas is dominated by either atomic or molecular hydrogen, depending on the overall density of the gas, which can range from  $10^2 \text{ cm}^{-3}$  in the more diffuse regions to upwards of  $10^4 \text{ cm}^{-3}$  in denser sources.

The study of interstellar dust has revealed much about its properties and proved to be an exciting study of small particles in situ. More surprisingly still, it is now clear that dust grains are a critical and active component of the Galaxy, and indeed of other galaxies. Dust grains play a part in establishing the thermal and chemical structure of interstellar clouds, in the collapse of these clouds in the process of star formation, and—of course—in the formation of planets, for which they are the raw material. We shall describe some aspects of the roles of dust in this article.

### 1.2. Evidence for dust

Box 1 lists the various ways in which astronomers obtain information about interstellar dust. The traditional approach has been through a study of interstellar extinction and how it varies with wavelength, from the near infrared to the vacuum ultraviolet. This curve has rather little structure except for a wide bump at a wavelength near 220 nm, and can be readily modeled by a distribution of dust grains of sizes ranging from a few nanometers to about  $1 \mu\text{m}$ . The grains are often assumed to be dielectric materials, such as silicates (for which there is infrared spectral evidence, see below), and carbonaceous material of various kinds is often included in such computations. In fact, these exercises do not give a unique solution because there are too many free parameters available to distinguish among different grain models.

Although these calculations are often carried out for grains that are assumed to be spherical, it is clear that some of them, at least, cannot be

#### Box 1. Methods of studying interstellar dust

1. General extinction curve of starlight in visible and ultraviolet.
2. Scattering and polarization of starlight.
3. Infrared absorption and emission features.
4. Re-radiation of absorbed starlight in infrared and millimeter-wave.
5. Depletions of elements from the gas phase.
6. Collection/analysis of interplanetary dust particles, especially the unprocessed component.

spherical. Starlight is often a few percent linearly polarized, and this is interpreted as being due to a selective extinction caused by dust grains that are partially aligned by the interstellar magnetic field. Thus, the interstellar medium acts rather like polaroid sunglasses, preferentially extinguishing one plane of polarization.

Starlight scattered by the dust can in some circumstances be detectable. These situations generally occur near to bright stars, and are called reflection nebulae. The variation of the scattered light with wavelength and with position in the nebula places a valuable extra constraint on the dust grain composition and size distribution, independently of the information contained in the extinction curve. However, accurate measurements of scattered light are rather difficult to make.

Atoms contained in dust grains are obviously not present in the gas! Some detailed information about the chemical (not physical) nature of the dust can be obtained by asking: what is missing from the interstellar gas? These “depletions” from an assumed standard stellar composition are very instructive indeed. Box 2 shows typical stellar abundances of selected atoms (with respect to hydrogen) along with the fraction of these atoms remaining in the gas phase in one particular cloud towards a bright star called Zeta Ophiuchi [2]. Some elements like iron, calcium, and titanium are very heavily depleted in this cloud; for example, less than one calcium atom in a thousand remains in the gas. Carbon is modestly depleted, but its total abundance is in fact very much greater than that of the metals, so the amount of carbon in the dust is quite large.

The most informative approach to determine the nature of the dust lies in infrared spectroscopy. This can only with great difficulty be carried out from the ground, because of the complications

introduced by the Earth’s atmosphere. The most accurate recent measurements have been made by a European satellite—the Infrared Space Observatory (ISO). The composition of cold and warm dust has been determined by ISO observations. Absorption by amorphous and crystalline silicates has been clearly identified, as has absorption by molecular ices including water, carbon dioxide, carbon monoxide, and methanol [3]. Fig. 2 shows an absorption spectrum of cold interstellar dust taken against continuum infrared radiation from an embedded stellar object within a dense cloud. The absorption features have been assigned in terms of molecular ice mantles and silicate dust cores. Warm dust shows spectral emissions of a range of features in the near- to mid-infrared that are characteristic of polycyclic aromatic hydrocarbons (PAHs) [4]. A typical emission spectrum is shown in Fig. 3. However, no identifications of individual PAHs have yet been made, nor is it clear whether the emitters are individual large molecules or assemblies of smaller molecules in a solid matrix.

The continuum re-emission of starlight absorbed by dust grains of a size comparable with the wavelength of visible light is detected by infrared observatories like ISO and by ground-based telescopes operating at millimeter wavelengths. This continuum emission is proving to be a very effective way of detecting the presence of interstellar matter, not only in our own Galaxy, but quite distant galaxies, too [5]. Dust has therefore been present in the Universe for a very long time, and the elements required for dust must have been formed rapidly in the early stages of the existence of the galaxies.

There is one further strand of information that helps us to determine the nature of interstellar dust. We can collect interplanetary dust as it falls

Box 2. Elemental depletions from the gas towards Zeta Ophiuchi

Element	Stellar	Depletion	Element	Stellar	Depletion
C	$2.1 \times 10^{-4}$	0.63	Cr	$3.2 \times 10^{-7}$	$1.1 \times 10^{-2}$
O	$4.6 \times 10^{-4}$	0.72	Fe	$2.7 \times 10^{-5}$	$7.1 \times 10^{-3}$
Mg	$2.5 \times 10^{-5}$	0.23	Ti	$6.5 \times 10^{-8}$	$4.2 \times 10^{-3}$
Si	$1.9 \times 10^{-5}$	0.09	Ca	$1.6 \times 10^{-6}$	$3.2 \times 10^{-4}$

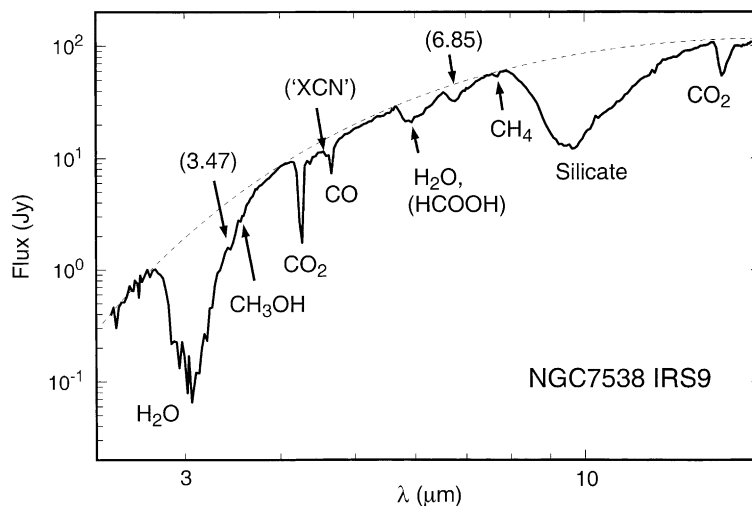


Fig. 2. The ISO spectrum of the embedded stellar object NGC7538 IRS9. The flux of radiation (in Janskys;  $1 \text{ Jy} = 10^{-26} \text{ (W/m}^2\text{)/Hz}$ ) is plotted against the wavelength in  $\mu\text{m}$  in the wavelength range 2.4–17  $\mu\text{m}$ . The spectrum shows absorption features arising from vibrations of various cold molecular species in the ice mantles and cores of dust grains. The dashed line is an estimate of the continuum. Uncertain (viz. 3.47 and 6.85  $\mu\text{m}$ ) or ambiguous assignments (viz. XCN and HCOOH) are in brackets. Taken, with permission, from volume 122 of the *Astronomical Society of the Pacific Conference Series*, 390 Ashton Avenue, San Francisco, CA.

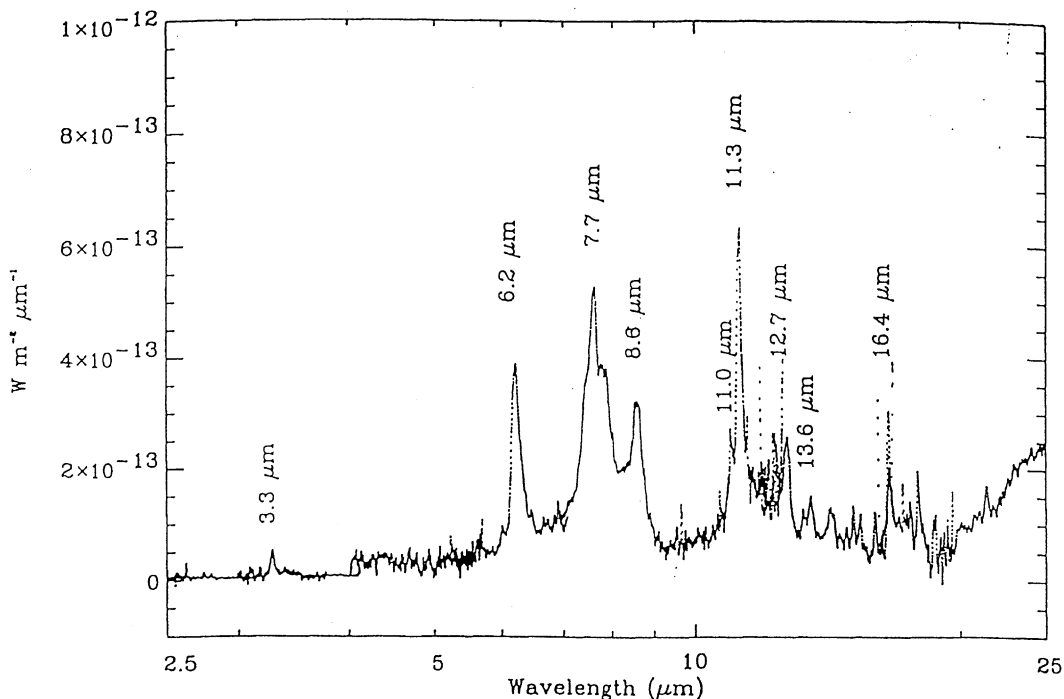


Fig. 3. The ISO spectrum of the warm reflection nebula NGC7023 plotted in terms of watts per square meter per  $\mu\text{m}$  vs. wavelength in  $\mu\text{m}$ . The spectrum shows emission features at wavelengths from 3.3 to 11.3  $\mu\text{m}$  normally interpreted in terms of the vibrations of PAHs. Taken, with permission, from C. Moutou et al. [23].

onto the Earth. In general, interplanetary dust comes from a variety of sources, including the erosion of asteroids and the impact of asteroids on planets. Such dust has been heavily affected by the physical processing the material has received. However, interplanetary dust also contains a component that seems to be unmodified; it shows no evidence of a high temperature phase, nor of shocks, and this component may be unmodified interstellar dust. Interstellar dust is expected to enter the solar system as it moves through interstellar space. Such dust was apparently identified by the Ulysses spacecraft, on its journey to the outer parts of the solar system [6]. Recent work by Bradley and co-workers has identified glasses with embedded metals and sulfides, or “GEMS”, that have a remarkable similarity in terms of physical and chemical composition and sizes with what is expected for interstellar dust [7]. Specifically, GEMS are typically 100 nm in size, and are mainly glassy with 10 nm-size globules of iron and nickel sulfides. Fig. 4 shows a picture of recovered GEMS. It is also interesting to look at the morphology of collected interplanetary particles larger than GEMS. Fig. 5 shows a rather large (10  $\mu\text{m}$ ) piece of dust obtained in the stratosphere with

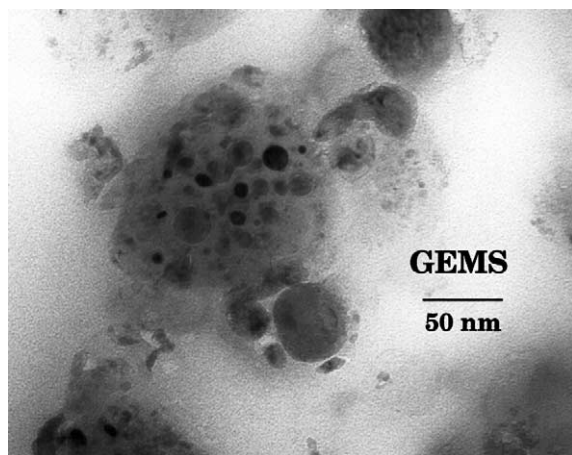


Fig. 4. Particles known as GEMS (glasses with embedded metal and sulfides). Usually a hundred nm in size, these primitive interplanetary dust particles are glassy with large numbers of smaller grains. Acknowledgment is made to NASA for allowing reproduction of this picture from web site <http://stardust.jpl.nasa.gov/science/sci2.html>.

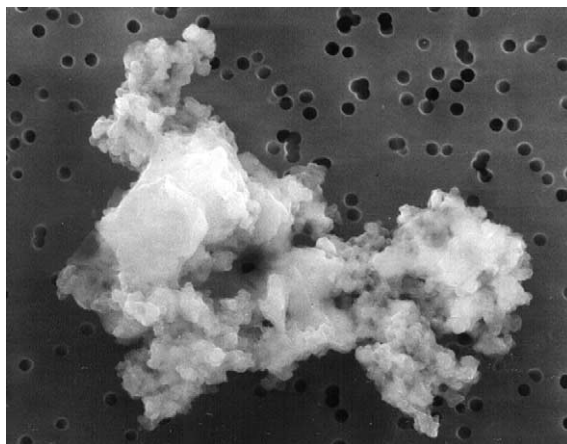


Fig. 5. A 10- $\mu\text{m}$  interplanetary dust particle known as a Brownlee particle. Collected in the stratosphere, it is composed of glass, carbon, and mineral silicates. Acknowledgment is made to NASA for allowing reproduction of this picture from web site <http://stardust.jpl.nasa.gov/science/sci2.html>.

portions containing carbon and different types of silicate minerals. This image may suggest what some of the larger interstellar grains may look like.

Information from all these strands leads to some uniformity of view as to the nature of interstellar dust, which is listed in Box 3.

#### Box 3. The nature of interstellar dust

1. Ranges in size from about 1 nm to 10  $\mu\text{m}$ , with many more small grains than large.
2. The larger grains are likely to be non-spherical, and perhaps porous, fluffy, and even fractal.
3. Composition is likely to contain cores of metallic silicates, carbonaceous material, and GEMS, probably in different populations rather than mixed in individual grains.
4. Mantles of ices ( $\text{H}_2\text{O}$ ,  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{CH}_3\text{OH}$ ) are found in cold dense regions.

## 2. Sources and sinks of interstellar dust

### 2.1. Where does the dust come from?

Hold a glass above a candle flame and it becomes covered in soot. The flame of the candle is quite evidently smoky, and sooty particles formed

somehow in the hot gas of the flame are expelled as the gas rises upwards against gravity. A similar process seems to be working in the atmospheres of hot stars. Towards the end of their lives, some stars develop rather extended atmospheres that may be cool and dense enough for solid nuclei to form. Then any atoms and molecules that are supersaturated will be rapidly deposited on these nuclei, forming solid particles. Radiation pressure from the central star is then capable of accelerating the dust and establishing an outflow in the entire dusty envelope, which travels out from the star until it mixes with the interstellar gas.

We do not fully understand the details of the nucleation process, whether in a stellar atmosphere or in a candle flame. However, this general picture for the formation of interstellar dust seems to be a valid one, for we can actually see in real time the formation of dust in a cyclic pulsation process in some stellar atmospheres. First, we see the rapid darkening of the underlying star as the dust forms abruptly in a runaway event; this is accompanied by a rise in the infrared emission from the star, as starlight is converted to heat in the dust. Then as the gas and dust drift away from the star, the effects of extinction are diluted, and the star shines brightly once again. Such outflows from stars are a fairly common phenomenon.

Outflows can be carbon rich or oxygen rich. This means that, after hydrogen and helium, the most abundant element is either carbon or oxygen, respectively. The stellar nuclear physics and the convective processes in the star determine the category to which the outflow belongs. The two types determine the nature of the dust that is produced. Where carbon is more abundant than oxygen, the oxygen is almost entirely locked up in carbon monoxide, and the excess carbon produces a rich chemistry of carbon-based molecules and of carbonaceous dust, i.e. sooty grains. On the other hand, where oxygen in an envelope is more abundant than carbon, the excess oxygen (after CO is formed) makes metallic oxides that nucleate to form solid oxides and silicates.

Cool stellar envelopes are not the only source of dust. Stellar explosions can also make a substantial contribution. Novae and supernovae are eruptions of stars near the end of their lives. An

eruption can eject a parcel of gas in which conditions may evolve in such a way that nucleation occurs and dust forms. This is often seen in a nova: first, the star brightens enormously; then it fades and the infrared emission rises as the dust is formed, and finally the star becomes optically bright once more as the dusty ejecta are dissipated.

In total, these sources inject into the interstellar space of our Galaxy about 30 000 times the mass of our Sun, in the form of dust, in each year. Similar processes occur in other galaxies, too. Will the Galaxy get more and more dusty, as time goes on?

## 2.2. *What happens to the dust?*

There is a limit to the amount of dirt (or dust) that the Galaxy contains, because there are “cleansing” processes in operation, too. The dust ejected from a star does not remain localized around that source, like a pall of smoke over a bonfire on a windless day. The interstellar medium is rather violently stirred by explosions of supernovae; these occur rather frequently in the Galaxy (perhaps more than once a century) and have Galaxy-wide effects. The explosions maintain a complicated density–temperature structure in the interstellar gas, and subject most of it to strong shocks which may have speeds as much as several hundred kilometers per second in the most tenuous gas, though slower, around 10 km/s, in the denser gas where most of the dust grains reside.

The probable fate of the dust is therefore destruction in shocks, via sputtering or shattering. For the grains of sizes that generate the interstellar extinction curve, the consequent lifetimes of dust are around 500 million years. This lifetime is just a few percent of the age of the Galaxy. So the dust that we detect now is really rather recent, in these terms! Somewhat larger grains, however, are affected more by shattering and their lifetimes are smaller by a factor of 10. However, in spite of all the supernovae and their associated shocks, about one-tenth of the dust in the interstellar medium at any time has not been shocked.

Starlight can also alter the chemical and physical nature of carbonaceous dust; for example, H-rich tetrahedrally bonded amorphous carbon is

converted under UV irradiation to an H-poor triply bonded form. The two forms have quite different optical and chemical properties. Similarly, crystalline silicates that may be a component emerging from O-rich stellar atmospheres can be significantly affected by the flux of energetic protons and electrons (the cosmic ray particles). The long-range order in the lattice is removed and the material becomes amorphous. Around young low-mass stars, dust particles coagulate into larger bodies, eventually forming primitive objects such as comets, and into the planetesimals that are the building blocks of planets.

### 3. Surface chemistry: the formation of molecular hydrogen

In dense interstellar clouds, a large number of molecular species have been identified in the gas phase via high resolution spectral techniques, chiefly rotational spectroscopy in the millimeter-wave region of the electromagnetic spectrum. These molecules range in complexity from  $H_2$  to a 13-atom linear nitrile,  $HC_{11}N$ , and are mainly organic in nature [8]. Many of the molecules are quite unusual by terrestrial standards and serve to show that our standard ideas on what molecules are stable and what molecules are not stable are biased by terrestrial conditions. Since hydrogen is the dominant element in the Universe,  $H_2$  is the most abundant molecule by far, with CO in second place, four orders of magnitude lower in concentration. More complex organic species are even less abundant, although the amount of material tied up in these species is very large compared with the analogous amount on our planet. How and where are the molecules formed?

Although the low density ( $n \approx 10^4 \text{ cm}^{-3}$ ), low temperature ( $T \approx 10 \text{ K}$ ) conditions in “dense” interstellar clouds do not appear to be favorable for chemistry, there is no real alternative to this local hypothesis. Interstellar clouds are formed from the detritus of previous generations of stars that blow out matter in the form of dust particles and gas. Despite the fact that molecules can indeed be formed in the ejecta of old stars, these molecules are “soon” (within about 100 years) torn apart by

the harsh ultraviolet radiation field found in interstellar space. So the gas-phase material forming interstellar clouds is essentially atomic in nature. Molecular synthesis then takes place over the eons despite the low densities and temperatures; the molecules formed by the in situ chemistry are protected from radiation to a great extent by the dust particles.

For more than 30 years, chemists and astronomers have investigated gas-phase formation and destruction routes for most of the molecules detected in the gas phase. The major reactions are exothermic ion–molecule reactions, since these are rapid and are known to occur even at very low temperatures. Atomic and molecular ions are produced in dense interstellar clouds via collisions with cosmic rays, which are particles (mainly protons) formed in supernovae and moving at relativistic speeds throughout the Universe. Simulations that include only gas-phase chemical reactions are successful in producing most ( $\sim 80\%$ ) of the molecules observed in the gas phase [8,9]. But there are some glaring exemptions, among which the dominant molecule  $H_2$  is clearly the most dramatic. This species cannot be formed when two hydrogen atoms collide in the gas, because the two atoms cannot stick together with high efficiency. Instead, the only feasible synthetic pathway involves the surfaces of interstellar dust particles.

Consider a hydrogen atom striking a low temperature dust grain. The sticking probability is known to be high for a variety of surfaces representative of the interstellar medium. An atom of hydrogen can stick to a grain, if not to another hydrogen atom, because the grain is a thermodynamic entity and converts the energy of collision into a rise in temperature. The surface formation of  $H_2$  can occur via two different routes. First, let us imagine a situation in which weak binding occurs between hydrogen atoms and the grain. An adsorbed H atom is then relatively free to diffuse over the grain either by tunneling from binding site to site or by thermally hopping over the barriers between such sites. The detailed nature of the diffusion has been investigated by many people, but appears to be very sensitive to the composition of the surface, including impurities. Since the

binding is weak, re-evaporation (desorption) into the gas phase is also possible, even if the temperature is very low. The formation of molecular hydrogen occurs when two diffusing H atoms approach one another and transfer enough of the energy of molecular formation to the grain that the H<sub>2</sub> species is stabilized. The newly formed molecule can desorb rapidly from the grain if some of the exothermicity of reaction can be channeled into translational motion perpendicular to the surface. Evaporation at a later time is also possible. The diffusive process is known as the Langmuir–Hinshelwood mechanism, and is probably the dominant interstellar process on surfaces such as silicates and amorphous ice. Following work of Salpeter and co-workers, astronomers had long thought that H atoms landing on grains move rapidly over the entire grain by tunneling from site to site; such rapid motions ensure that there is a high efficiency of forming H<sub>2</sub> despite the possibility of evaporation [10]. Within the last several years, however, detailed experimental measurements on the diffusive formation of H<sub>2</sub> have been carried out at low relevant temperatures [11] on olivine and amorphous carbon. It was found that diffusion of H atoms occurs much more slowly than envisaged by astronomers and that it occurs mainly by thermal hopping rather than tunneling. It was also found that the newly formed H<sub>2</sub> is desorbed from the cold surface a significant percentage of the time. Taking into account the new laboratory results, it still appears that, under interstellar conditions, H<sub>2</sub> can be formed by a diffusive mechanism on a surface such as olivine, but the temperature range over which this can happen is much smaller than previously assumed. At lower temperatures, diffusion does not occur efficiently, while at higher temperatures, evaporation occurs before reaction.

An alternative possibility for surface H<sub>2</sub> formation occurs if the H atoms are bound sufficiently strongly to the surface that diffusion is not competitive. In this case, evaporation is also unlikely to be important, and interstellar grains will “rapidly” form monolayers of atomic hydrogen. The formation of molecular hydrogen can then occur via an Eley–Rideal mechanism, in which a gas-phase hydrogen atom lands atop a surface

hydrogen atom, forming a molecule which leaves the grain surface. Although experiments on such a mechanism have yet to be undertaken, theoreticians have been quick to join the fray. Fully quantum calculations on a material with the properties of graphite show that H<sub>2</sub> formation can occur via an Eley–Rideal mechanism [12].

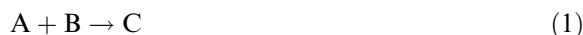
Although the exact mechanism of H<sub>2</sub> formation on grains is still uncertain, the total conversion of atomic to molecular hydrogen can occur on grain surfaces in a time of  $\sim 10^5$  years if it is assumed that nearly all H atoms that land on grains eventually form H<sub>2</sub>. The time of  $10^5$  years is relatively short in an astronomical sense, but this time scale could be much longer if the formation of H<sub>2</sub> on grains is much less than 100% efficient. The actual astronomical efficiency is, of course, highly uncertain. Clearly, astronomers need help from scientists more knowledgeable in surface science!

#### 4. Surface chemistry: the formation of other species

Molecular hydrogen is not the only species that can be formed at low temperatures on the surfaces of interstellar grains. If hydrogen atoms diffuse rapidly over a grain surface, they can interact not only with other hydrogen atoms, but with heavier species as well. Although more slowly moving than H atoms, heavier species can also react with one another. In a low temperature medium, the reactive species are likely to be limited in the main to atoms and radicals since they can react with zero or at most small activation energy. Positively charged species, which form in the interstellar gas, are likely to be neutralized when they strike granular surfaces because the surfaces are thought to be negatively charged given the greater thermal velocity of electrons compared with positive atomic and molecular ions. There is the usual astronomical uncertainty in this argument. Neutralization can also occur on neutral grains via resonant or Auger processes.

Unlike the gas phase, most reactions occurring on the grain surfaces are thought to be associative in nature, like the formation of H<sub>2</sub>. If we consider two reactive species A and B, an association

reaction is one in which only one product, labeled C, is formed:



while a “normal” reaction produces more than one product. The difficulty in producing only one product is that the species A and B must literally stick together. In the gas, this sticking can occur by the emission of excess energy via radiation (“radiative association”) or, at sufficiently high densities, via an inelastic collision with a third body. On a grain surface, the grain acts as the third body so that energy is always being taken out of the reactive system. Thus, it is expected that “normal” reactions on grains will occur only if there is no association product with a strong chemical bond between A and B. The competition between associative and normal reactions is not fully understood, but some work has recently been undertaken on this subject [13].

Some of the types of (exothermic) surface reactions that can occur under interstellar conditions are shown in Box 4.

Box 4. Types of grain surface reactions in interstellar clouds

- |       |                              |
|-------|------------------------------|
| (i)   | $H + X \rightarrow HX$       |
| (ii)  | $X + Y \rightarrow XY$       |
| (iii) | $H + HX \rightarrow H_2 + X$ |
| (iv)  | $H_2 + X \rightarrow H + HX$ |

The first type is obviously analogous to molecular hydrogen formation. Among the salient reaction pathways occurring via sequences of reactions of type (i) are the hydrogenation of O, C, N, and S into the saturated forms  $H_2O$ ,  $CH_4$ ,  $NH_3$ , and  $H_2S$ , all formed much more efficiently than in the gas phase. An example of reaction type (ii) is the formation of  $CO_2$  from CO and O. Reaction class (iii) contains processes such as the abstraction of a hydrogen atom when H reacts with  $H_2S$  to form  $H_2$  and HS with a small activation energy. Finally, an example of reaction type (iv), which always occurs with some activation energy, is the hydrogenation of OH via  $H_2$ :  $OH + H_2 \rightarrow H_2O + H$ . Although as dense clouds mature,  $H_2$  becomes far more abundant than H in the gas phase ( $H/H_2 \sim 10^{-3}$ – $10^{-4}$ ), the reactivity of atomic hydrogen on

grains is such that it is still the dominant reactive partner.

One very important sequence of reactions in class (i) is the slow hydrogenation of surface CO into methanol via successive reactions with atomic hydrogen:  $CO + H \rightarrow HCO$ ;  $HCO + H \rightarrow H_2CO$ ;  $H_2CO + H \rightarrow H_3CO$ ;  $H_3CO + H \rightarrow CH_3OH$ . There are competitive normal channels and there are activation energy barriers for several of the reactions along the pathway. Yet low temperature laboratory work and theory indicate that the production of methanol may take place [13].

All of the above reaction types occur in interstellar clouds if the mechanism for surface chemistry is indeed diffusive in nature. If, however, the Eley–Rideal mechanism dominates, which reactions are important has yet to be even guessed at. One class of dust particles for which this latter mechanism is likely to be operative are those particles considerably smaller than the standard size of  $0.1 \mu m$  yet too large to be thought of as gas-phase molecules. For such small particles, weakly bound adsorbates are likely to be desorbed efficiently by an assortment of thermal pulses, and chemical bonds between adsorbate and particle are more likely to be formed, so that strongly bound species may dominate [14].

## 5. Interstellar surface chemistry: simulation

In order to model the chemistry of interstellar clouds, astronomers have to follow the chemistry occurring both in the gas-phase and on the surfaces of the dust particles. The gas-phase chemistry is typically treated via rate equations. Consider a gas-phase species C that is one product of a reaction between A and B and is destroyed by reaction with D. Its rate equation is given by the expression

$$d[C]/dt = k_{A-B}[A][B] - k_{C-D}[C][D] \quad (2)$$

where the symbol [ ] refers to concentration, and the  $k$ 's are so-called rate coefficients. If surface chemistry could be ignored the solution of the gas-phase chemistry could be undertaken by simultaneous integration of rate equations for all species in the model given initial concentrations and either fixed or varying physical conditions. Such

simulations have been done, although they are not 100% gas-phase in nature since they contain high abundances of  $H_2$  as an initial condition. The result is a series of time-dependent concentrations which for many molecules at selected times are in reasonable agreement with what is observed. But the dust cannot be ignored! The existence of dust particles leads to two new terms on the right-hand side of Eq. (2)—one for loss of C onto the surface (adsorption) and one for desorption of surface C back into the gas phase. At the low temperatures of most regions in interstellar clouds, thermal evaporation of adsorbates within even astronomical time scales is limited to light species such as H,  $H_2$ , and He. Several intermittent sources of energy have been suggested to cause non-thermal desorption, including grain–grain collisions, cosmic ray bombardment, the exoergicity of chemical reactions, and photons. The efficiency of these mechanisms does not appear to be high, so that in the absence of star formation (which raises the temperature or causes shock waves) adsorption eventually triumphs for heavy species, the gas phase molecules decline in concentration, and large mantles inexorably build up on the interstellar grains. Of course, “eventually” is a long time even in astronomy, and gas-phase abundances can remain high for quite some time!

The mathematical treatment of surface chemistry depends on the operative mechanism, which we here assume to be diffusive. Consider the surface of a grain with large numbers of diffusive and reactive species. If we once again consider a species C that is formed by reaction of A and B and destroyed by reaction with species D, we obtain an analogous rate formula of the type

$$dN_C/dt = K_{A-B}N_A N_B - K_{C-D}N_C N_D \quad (3)$$

where the symbol  $N$  stands for the number of molecules of a particular species on the surface. The rate coefficients  $K$  are quite different from their gas-phase counterparts since they depend on diffusion rather than simple straight-line motions, as in the gas. If we assume that diffusion occurs via thermal hopping from site to site, the rate coefficient  $K_{A-B}$  can be expressed via the relation [15]

$$K_{A-B} = \kappa \{v_A \exp(-E_A/kT) + v_B \exp(-E_B/kT)\} / N_{\text{tot}} \quad (4)$$

where  $v_A$  and  $v_B$  are surface vibrational frequencies for A and B, respectively,  $E_A$  and  $E_B$  are energy barriers against diffusion from one binding site to another for A and B, respectively,  $k$  is the Boltzmann constant,  $T$  is the temperature,  $N_{\text{tot}}$  is the number of binding sites on the surface, and  $\kappa$  is a coefficient expressing the likelihood of reaction if species A and B approach one another closely. The parameter  $\kappa$  is assumed to be unity for exothermic reactions unless there is an activation energy barrier against reaction, in which case  $\kappa < 1$  is determined by the greater of the tunneling or hopping probability. The frequencies multiplied by Boltzmann factors give the rate per second of hopping to an adjacent binding site. Upon substitution of the expression for  $K_{A-B}$  into Eq. (3), one can see that the overall rate of formation of C can be thought of as the sum of two terms—one involving the diffusion of A and the other that of B. For A, the term consists of the probability per unit time that species A moves from one binding site to another multiplied by the probability ( $N_B/N_{\text{tot}}$ ) that the neighboring site is occupied by B, multiplied by the number of species A on the surface, multiplied by the probability of reaction upon a close encounter of A and B. A similar term, with equally many factors, exists for B. The destruction of species C by species D can be similarly formulated. The rate law for surface species C in Eq. (3) has to be modified, if gas-phase species are included, by appropriate terms for adsorption onto and desorption from the surface.

Do these rate laws for surface chemistry pertain to diffusive surface chemistry on interstellar grains? Not with any certainty! The basic problem is that grains are small, and large numbers of reactive species may not be present at any given time. If, on average, the number of species A on a grain is significantly less than unity, it is not at all clear that the abundance of A is determined by its rate of diffusion on the grain. Consider, instead, the so-called accretion limit: species A lands on a grain, species B lands thereafter, and before a third species can land, A and B react to form C. The rate of production of C in a given time interval is not

dependent on the diffusion rates of A and B as long as they are fast enough to cause reaction before the third species lands on the surface. In this instance, it is closer to reality to avoid the use of rate equations and to utilize a Monte Carlo approach, in which the order of successive landings on a particular grain is calculated probabilistically, and reaction is assumed to occur before another landing if the species are (a) reactive and (b) capable of diffusing rapidly. One problem with this approach, however, is that the accretion limit is not always applicable.

Because the Monte Carlo approach has not yet been successfully introduced into a true time-dependent calculation, simulations of grain chemistry (often coupled with gas-phase chemistry) using rate equations are much more common, even if of uncertain value. For truly simple systems in which the gas-phase abundances of a small number of species are held fixed although the species are allowed to accrete onto grains, the rate equation method can be tested against the Monte Carlo approach in the accretion limit. Such a comparison shows that when a cloud evolves to the point that much of the gas-phase atomic hydrogen has been converted into molecular hydrogen, the remaining rapid processes occurring on dust surfaces may not be handled well by the rate equation approach. In particular, for grains at a temperature of 10 K, it is found that for a limited system of O and H atoms adsorbing onto grains, the rate equations tend to produce too much H<sub>2</sub> and not enough O<sub>2</sub> under some conditions [16].

Some semi-empirical modifications of the rate equation method for grain surface chemistry have been formulated that allow the results of this approach to agree with the results of the Monte Carlo method in the limit that the latter approach is correct (the accretion limit) [16]. The original formulation has since been modified. For the simple O, H system, one must limit the diffusion rates of H and O so that they do not exceed the larger of the evaporation and accretion rates for each atom. The correction is much more important for the faster-moving H. These suggested modifications have not met with universal praise, but providence has been merciful to their authors. The recent experimental work concerning the forma-

tion of H<sub>2</sub> on olivine indicates that the diffusion rate of H is sufficiently slow that the proposed modification is barely necessary at 10 K, so that the simple rate method may be a reasonable approximation after all.

What do the admittedly imperfect simulations of surface chemistry tell us? This depends on the physical conditions of the astronomical source and how they change with time. As long as a region remains cold and free of shock waves, mantles containing an assortment of ices grow due both to surface chemistry and to adsorption from the gas. Other regions experience a sufficient warming up due to star formation that the mantles are lost. The molecules ejected into the gas then strongly affect the gas-phase chemistry, as we shall see.

## 6. Interstellar ices

Stars and star-forming regions often emit enough infrared radiation to act as spectroscopic light sources. Their emission can be partially absorbed by cold material in dense clouds between them and us. The absorption is in the form of sharp features, attributable to gaseous molecules, and, as mentioned earlier, broad features, attributable to molecules both in the cores of dust particles and on their surfaces. Some broad features and their assignments are shown in Fig. 2. The broad absorption spectra, when coupled with laboratory simulations, tell us the species responsible for the absorption, the relative abundances of the species, and even the environments in which the molecules are located. Since the features are broad, one must be careful about definitive assignments, but it must be realized that strong features can only be carried by molecular species that contain the more abundant elements present in the Universe.

One of the best-studied objects lies in the direction of the so-called “field star” Elias 16, for which the line of sight passes through dense interstellar material in the constellation Taurus [17]. The strongest mantle features seen in the spectrum belong to water ice, which is estimated to contain much of the elemental oxygen available (roughly 10<sup>-4</sup> of the abundance of hydrogen) and to

comprise up to 100 monolayers of material per grain. Next in abundance come CO and CO<sub>2</sub> (dry ice), which constitute 25% and 22% of the water ice, respectively. The CO is divided into two environments—an apolar environment (22%) and a polar one (3%).

More commonly, infrared absorption spectra arise from cool gas and dust in front of IR-emitting young stellar objects (“protostars”) within dense interstellar clouds. The spectrum in Fig. 2 is of this type. These protostars tend to warm up the area around them so that the physical conditions in the foreground absorbing regions are neither as well characterized nor as homogeneous as when the source of the infrared radiation is a background field star. Still, the existence of ices in these regions implies that temperatures are quite low ( $\ll 100$  K). In addition to the H<sub>2</sub>O, CO, and CO<sub>2</sub> seen towards Elias 16, significant abundances of methanol, methane, formaldehyde, OCS, and formic acid are present in grain mantles.

Whatever the source of the radiation, the derived abundances of at least some of these surface species, especially water, CO<sub>2</sub>, and CH<sub>3</sub>OH, are much too high to be explained by gas-phase processes followed by adsorption within reasonable time periods. Consequently, it would appear that surface chemistry is needed to explain their abundances, and excellent laboratory work supports this interpretation [18]. Currently, detailed simulations of gas-phase and diffusive grain chemistry in dense cold regions are able to produce large abundances of water ice, carbon monoxide, and methanol, but do not appear able to explain the large abundance of dry ice (carbon dioxide) [19].

Surface chemistry can be activated by photochemical energy or the bombardment of high-energy particles such as cosmic rays. Laboratory groups have shown that high doses of radiation or particulate bombardment can indeed enhance the production rate of CO<sub>2</sub> and many other molecules [18]. In addition, with suitable starting materials, large abundances of refractory organic species can be produced. The question remains as to whether these results are pertinent to the much lower photon and particulate fluxes present in interstellar clouds, even in the vicinity of newly formed

stars. Simulations of both laboratory and interstellar photochemistry are clearly needed.

Finally, when many monolayers of ices are present, reactants need not remain on the surface but can diffuse vertically into the mantle. Chemistry can then occur underneath the surface.

## 7. Protoplanetary disks, comets, and planets

In recent years, astronomers have spent much time studying the formation of low-mass stars analogous to the sun. As dense cores within large interstellar clouds collapse to form such stars, they develop so-called “accretion” disks of gas and dust that revolve around a central object. The circular disks, which are quite planar in nature close to the central star, are sometimes referred to as protoplanetary, since it is thought that they will evolve eventually into solar-type planetary systems. Protoplanetary disks are typically much larger than our solar system, but the material in the inner portions is gradually accreting inwards as it revolves around the central object. The densities are much higher than in normal interstellar clouds, especially in those regions close to the newly forming star. In the mid-plane of a typical disk, much of the gas-phase molecular material has already been adsorbed onto the dust particles.

Simulations of the chemistry occurring in protoplanetary disks must start with a portion of a dense interstellar cloud, follow the gas-phase and surface chemistry during collapse into the disk phase, and then follow the chemistry occurring in the disk. A variety of groups have carried out such calculations (e.g. Ref. [20]) but only recently has surface chemistry been included in the models. The simulations show the inventory of both gas-phase and surface molecules to be strongly dependent on the age of the protoplanetary disk and the position in the object. The results for the outer regions can be compared with radioastronomical observations of the gas-phase molecules, while the results for the inner regions, where the gas phase is heavily depleted, can be compared with molecules found in primitive solar system bodies such as comets.

One of the most interesting recent cometary observations concerns the deuterium-to-hydrogen

elemental abundance ratio in the cometary molecules HCN and H<sub>2</sub>O. The ratios DCN/HCN and HDO/H<sub>2</sub>O are several orders of magnitude higher than the elemental D/H ratio seen in most bodies of the Universe, an effect known as fractionation. The fractionation seen in molecules in cold interstellar clouds is even stronger than in comets due to a variety of gas-phase and surface chemical processes. Models of protoplanetary disks show that much of the fractionation detected in interstellar clouds is preserved on the surfaces of dust particles in the inner regions of disks, which are presumably the forebears of comets [21].

## 8. Hot cores

The formation of high-mass stars leads to some spectacular events. It also leads to some more prosaic happenings, among which are so-called “hot cores”, named imaginatively after the first such object, seen in the Orion dense interstellar cloud. Hot cores are small ( $\approx 0.3$  light years), dense ( $n \approx 10^6$ – $10^7$  cm<sup>-3</sup>), and warm ( $T \approx 100$ – $200$  K) clumps of material, in which the molecular material in the gas phase is noticeably different from that in cooler regions of dense interstellar clouds. In particular, small saturated molecules such as NH<sub>3</sub>, H<sub>2</sub>O and methanol (CH<sub>3</sub>OH) are far more abundant than in the ambient medium, while larger organic molecules such as methyl formate (HCOOCH<sub>3</sub>), dimethyl ether (CH<sub>3</sub>OCH<sub>3</sub>), ethanol (C<sub>2</sub>H<sub>5</sub>OH), and ethyl cyanide (C<sub>2</sub>H<sub>5</sub>CN) are seen only in such regions. The detection of large abundances of ethanol in hot cores was particularly noticed by the press, with headlines such as “pub at the end of the Universe” and “Scotch on the rocks.” The detection of somewhat larger species than currently seen in hot cores (methyl-ethyl ether, diethyl ether, ethyl formate, etc.) is not yet feasible because the laboratory spectra in the relevant spectral ranges used by radioastronomers to detect molecules have not been studied sufficiently.

The dominant, perhaps even correct, school of thought is that the molecules detected in hot cores arise from chemical processes occurring both before star formation proceeds and during this pro-

cess. Before the onset of the collapse leading to star formation, gas-phase and surface chemistry proceed under typical interstellar conditions ( $n \approx 10^4$  cm<sup>-3</sup>,  $T \approx 10$  K). Mantles containing hydrogen-rich ices are synthesized on grains, with atomic hydrogen playing the main role in the hydrogenation leading to H<sub>2</sub>O, NH<sub>3</sub>, CH<sub>3</sub>OH and other species. During star formation, the temperature gradually rises to 100–200 K and the grain mantles evaporate into the gas. Some grain chemistry may also occur during the heating up period, especially involving species in the inner mantle, which desorb relatively slowly. There follows a “high” temperature gas-phase chemistry that takes roughly 10<sup>5</sup> years to expunge the initial conditions and reach a new steady state. During this period, gas-phase reactions are thought to convert a significant proportion of the liberated methanol into more complex organic alcohols (e.g. ethanol), ethers (e.g. dimethyl ether), and other classes of molecules [22]. Thus, what one detects is the result of both a previous era of low temperature surface chemistry and a more recent era of gas-phase chemistry. Selected molecules such as H<sub>2</sub>S can even be used as clocks of the ages of the hot core regions.

Hot cores are not identical in chemical composition. In addition to the effect of age, there are also much greater differences that must reflect different surface processes from the previous cold era. For example, in the Orion molecular cloud, there are two closely spaced hot cores, one of which (The “Compact Ridge”) shows higher abundances of oxygen-containing organics while the other (The “Hot Core”) shows higher abundances of nitrogen-containing species. One possibility for explaining these chemical differences is that during the cold era the Hot Core was somewhat warmer than the Compact Ridge so that gas-phase CO could not reside on grain surfaces long enough to be hydrogenated into methanol, the precursor of oxygen-containing organics.

One molecule of extreme interest because of its association with life is the simplest amino acid—glycine. Despite much effort, however, glycine has not been detected unambiguously in hot cores. Of course, looked at more rationally, regions around young high-mass stars are not likely

to form life-sustaining or even giant planets since high-mass stars live for only relatively short periods of time. Thus, the idea of an association between biology and hot cores is unlikely.

## 9. Unsolved problems and future prospects

Goethe once wrote that “We know accurately only when we know little; with knowledge doubt increases.” For many years, many if not most astronomers assumed with little experimental basis to support them that molecular hydrogen was formed on the cold surfaces of interstellar dust particles but that the formation and depletion of almost all other molecules could be understood without reference to dust particles. This view is now untenable as the importance of dust particles and their surface chemistry becomes better appreciated if not yet totally understood. Yet, at the same time, what we thought we knew about the formation of H<sub>2</sub> turns out to be an unrealistic simplification of a process which depends intimately on details we do not yet know accurately, such as the shape of interstellar dust particles, and their detailed chemical nature.

Given the current intense interest in H<sub>2</sub> formation on cold surfaces and the number of experiments now existing or being set up to understand the chemistry, we can expect that in the next few years, we will have a detailed understanding of the various ways in which H<sub>2</sub> can be made on assorted cold surfaces in the laboratory. We may even have experiments involving small particles rather than larger surfaces. At the same time, our understanding of the physical and chemical nature of dust particles is likely to improve, as new techniques and satellites for observing dust are brought into play. Perhaps within the next decade, the interstellar H<sub>2</sub> problem will be solved.

Of course, the chemistry of H<sub>2</sub> is not the only chemistry that occurs on the surfaces of interstellar dust particles. Many other reactions occur as well, and experiments on some of these are being undertaken. Our knowledge of types of reactions, especially hydrogenation processes, will soon be much greater than it has been up to now, and this increasing knowledge will enable astronomers to

understand the chemistry of interstellar clouds in far more detail.

We now know that surface chemistry is not confined to the Earth, but is a widespread phenomenon throughout the Universe. The surface is provided by interstellar dust particles, which are very small and highly varied. Despite their distance from us, we have learned much about them. We also know that some very abundant molecules—especially molecular hydrogen—are formed on their surfaces, although the exact nature of how the formation occurs still eludes us. It is indeed a dusty Universe, and the ubiquitous presence of the dust means that it is also a Universe filled with surface science.

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